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## Nanocomposite Fibers

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### ABSTRACT

Nanocomposite fibers involve the concept of integrally dispersing nanosized particles of the second phase inorganic material into fiber forming polymers such as nylon or polyester. The material goal involves obtaining bi-phasic fibers with high mechanical stiffness and strength, electrical conductivity and/or enhanced other features such as thermal stability. Thus far, the main difficulties toward achieving nanocomposite fibers are: (1) the inability of obtaining large quantities of nanoparticles in a pure, unagglomerated state and (2) obtaining a uniform, intimate dispersion of single entity nanoparticles in a fiber polymer matrix. These problems have been approached in the context of studying the properties of experimentally prepared nano-silica reinforced fibers and attempts to prepare carbon nanotube, CNT, containing fiber material. Modulus and tenacity tests on experimentally prepared nanosilica filled PET (polyethyleneterephthalate) fibers showed the silica nanoparticles reduced the modulus and tenacity (tensile strength) of the filled PET fiber materials. DSC and shrinkage studies on nano-silica/PET fiber show that polymer crystallinity is influenced by the presence of the silica nano-particles. Heats of melting are found to increase as the filler loading increases. In further shrinkage studies, the "shrinkage modulus" of these nanosilica/PET fibers was found to increase by the addition of silica nanoparticles. Attempts to prepare nylon reinforced CNTs (multi-wall) from a commercially available CNT/nylon resin "concentrate" failed due to the poor melt dispersion processing of the blended polymer. Only very weak CNT reinforced nylon fibers could be prepared.

### INTRODUCTION

This paper focuses on the understanding of creating nanocomposite Fibers. Here one must determine ways of intimately blending individual entities of nanofibers, such as carbon nanotubes and SiC whiskers, silica and clay, into polymers with the goal of producing new forms of textile fibers. The properties of these presumed nanocomposite fibers are widely different from the spectrum of fiber forming polymers that now exist. One might expect the modulus and strength of existing fiber polymers to be greatly enhanced by the addition of nanofiber reinforcement. For example, if carbon nanotube (CNT) particle implanted fibers are used, one would expect a great increase in the electrical conductivity of the so-reinforced fibers since CNTs themselves are electrically conducting. Nanofiber particle reinforced fiber polymers such as nylon, polyester, acrylic, cellulose etc. are the more obvious fiber composites to study as the more traditional choice of fiber producing polymer. However, the fabrication of nanocomposite fibers from these polymeric media is not a direct process.

## EXPERIMENTAL DETAILS

### 1. General Sources of Nanoparticles and Other Materials

- (1) Carbon Nanotubes (CNT) –CarboLex AP, Carbolex Inc. Lexington, KY; Graphite Nano-Fibers, (GNF), Catalytic Materials, LLD, Holliston, MA
- (2) Nano-Silica Filled PET Fibers - Supplied by Albany International, Mansfield, MA
- (3) 20% Concentrate of multiwall CNTs in nylon 66 – Fibril® nylon 66, Hyperion Catalyst Inc. (HCI), Cambridge, MA
- (4) 15% Concentrate of multiwall CNTs in polybutyleneterephthalate Fibril® (PBT) from HCI
- (5) Graphitic Carbon Black - Black Pearls 2000, Cabot Corp., Boston, MA

The nanosilica/PET blended fibers were prepared from in-situ polymerized with varying nanosilica loading of 1%, 1.5%, 3% and 5% by extruding in a twin screw extruder. These prepared fibers were used in the study. Studies were conducted in an effort to determine if commercially available CNT “concentrated” manufactured by Hyperion Catalysts, Inc (HCI), Cambridge, MA could be formulated to form fiber producing polymer material. To this end, nanotubes (multiwall CNTs) in a 20% nylon concentrate form (Nylon 66, Fibril™) and PolyButyleneTerephthalate (PBT) in a 15% CNT concentrate form (PBT Fibril™) were obtained. The approach was to compound these HCI concentrates with virgin (fiber grade) nylon or PBT resin to form CNT containing resin molding compounds having good electrical and mechanical properties. These compounded materials were extruded into fibers.

## DISCUSSION

### Novel Carbon Nano-Particles

Catalytic Materials, Ltd., Holliston, MA has developed a process for the synthesis of a similar material to carbon nanotubes, “tubular” graphite nano-fibers (GNF), which are produced from the decomposition of carbon monoxide/hydrogen mixtures over selected metal surfaces at temperatures over the range 600 to 750°C [1]. It has been found that by judicious choice of the catalyst and control of the parameters involved in the synthesis, it is possible to control the morphology and the crystallinity of the structure [2]. High-resolution transmission microscopy studies have revealed that GNF consist of well-ordered graphite platelets, aligned at various angles with respect to the fiber axis. We can now produce “faceted tubes”, “ribbons”, “platelets” and “herring-bone” conformations, which are generated by the correct choice of catalyst system and reaction conditions [3-6].

### *Nanoparticle Reinforced Fibers*

#### *PET/Silica Nanocomposite Fibers*

The polymer material properties of PET/nanoparticle silica composites were studied. Nanocomposite fibers made from several blends of PET/Silica (Nyacol DP6100, average particle diameter = 100 nm or less) were acquired from Albany International,

Mansfield, MA. DSC measurements were carried out on the polymer/silica blends containing 0% (neat PET), 1.5%, 3% and 5% (by weight) silica. Here, the crystallization endotherm temperature was not significantly changed by the presence of the various weight concentrations of silica. Endothermic peak (melting) temperatures ranging from 252 to 254°C were observed. Also the general shapes of all the DSC curves were not too much different from each other. However, upon further analysis, a trend was found in the (normalized) heat of melting,  $Q_m$ , of these composites. Correcting the determined heat of melting according to the percent polymer mass in the nano-composite fiber, created a linear trend in the data as shown in Figure 1.  $Q_m$  is found to increase as the concentration of the silica increases. This suggests that the silica-PET interfacial (boundary layer phase) material formed in these composites has a strong influence on the heat of fusion. Hence, the higher loading of nano-silica composite fiber has a higher interfacial area than that of the "neat" PET polymer. In turn, heat of fusion increases as the filler loading increases.

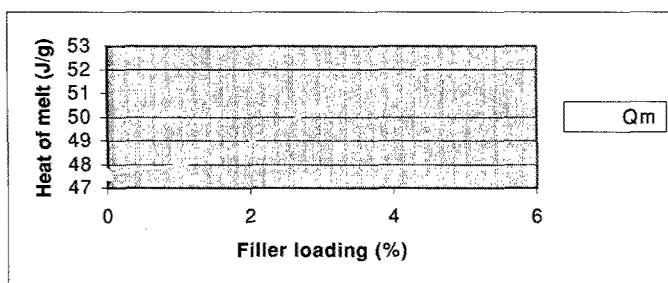
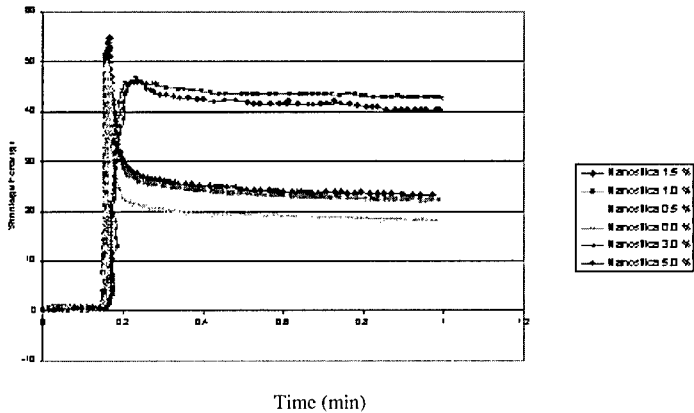


Figure 1. Effect of Filler on Heat of Melting,  $Q_m$ , of PET/Silica Nanocomposite Fibers

In additional work, the tensile modulus and inherent shrinkage of nanosilica/PET (figure 2) composite fibers were measured for filler loadings of 0.5, 1, 1.5, 3 and 5% (by weight). The average force and shrinkage of all the samples were measured using the FST 2000 apparatus (Lawson and Hemphill). Dispersion of the nanoparticles within the polymer matrix was observed through polarized light microscope and SEM. The silica nanoparticles were found to be well dispersed. The shrinkage test involves securing a yarn or fiber sample at a fixed length, in a constant temperature chamber under a constant load. The shrinkage peak force can be better explained as an intrinsic property of the polymeric fiber and the 'treatments' imposed during fiber spinning process. Fiber formation process generally occurs in three broad stages flow deformation, crystalline orientation and plastic deformation. The crystalline orientation of polyethyleneterephthalate (PET) occurs very rapidly accompanied by neck-like deformation and release of latent heat. Higher filler concentrations may induce "additional" crystallinity in the fiber as evident in higher silica loading. At the high temperatures there appears to be a rapid change in the fiber's fine structure that determines its properties. There is a change in degree of molecular orientation that may have arisen out of interaction between filler and fiber matrix. A frozen-in stress contributes greatly to peak force. Many molecules of the materials become frozen in an

oriented conformation. Such a conformation is unnatural to “neat” polymer molecules, which continuously strive to take up a randomly coiled state. So there is a frozen-in stress corresponding to frozen-in strain due to molecular orientation to enhance the peak force. Another factor that corresponds largely to the peak force is the defects in the fiber yarn or there may be a very poor dispersion of the silica in the molecular level to avoid the defects in 0.5% loaded composite fiber.

In additional experiments, all the samples were held at 177 °C for 2 min and then allowed to come down to room temperature and then shrinkage of the samples were measured. To our expectation, no shrinkage was observed in any case. Under high temperature (177 °C), all the samples underwent a molecular re-orientation process, an annealing, that resulted in reducing the entropy of the system and fiber shrinkage at lower temperature comes to nil. Heating the samples to 177°C perhaps takes care of induced orientation suppressing the marginal effect of fillers towards crystallization. However, crystallinity is not the only factor that could be responsible for reduction in shrinkage. Larger crystallites and a lower degree of orientation in the amorphous zone leads to reduced shrinkage. The mechanism of nanocomposite fiber shrinkage phenomena is still under investigation.



**Figure 2.** Variation of shrinkage force of the composite fiber with time

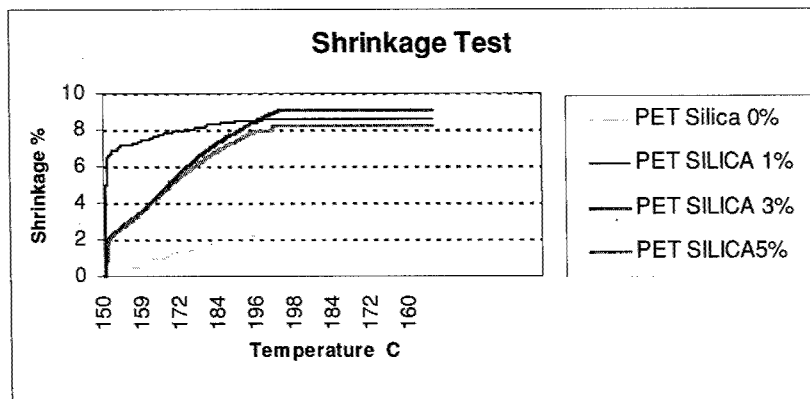
**Table1** Mechanical properties of PET/nanosilica composite fibers

| Denier | Tenacity<br>(g/den) | Modulus<br>(g/den) | %elongation | Silica loading<br>(% wt) |
|--------|---------------------|--------------------|-------------|--------------------------|
| 240    | 4                   | 120                | 26          | 0                        |
| 240    | 3.85                | 100                | 28          | 1                        |
| 240    | 3.95                | 90                 | 26          | 1.5                      |
| 420    | 3.11                | 30                 | 50          | 3                        |
| 420    | 3.23                | 36                 | 55          | 5                        |

Additional amorphous content with increase in silica loading is probably responsible for increase in elongation at break and observed decrease in modulus of the samples as silica loading increases. The original crystalline melting point decreases marginally with filler loading however normalized melting energy increases. This may well be because of increased amorphous content with increased nanosilica in PET/silica nanocomposite.

### ***Shrinkage Vs temperature of PET/silica nanocomposite fibers***

The shrinkage of the PET/nanosilica was measured in FST 3000 force shrinkage tester from 150°C to 200°C at 5°C/min ramp and then cooled to 150°C. As shown in figure 3 the shrinkage of the PET fibers increases with increasing filler loading and the fibers with highest filler loading shows the maximum shrinkage value. Owing to very small size large number of amorphous nanosilica molecules may give rise to increased non-crystalline area at the polymer-filler interface. This extent of formation of such non-crystalline region increases with increase in silica loading and probably that contributes to the increase in percentage shrinkage value with increased filler loading. Once we heat the samples it seems that non-crystalline regions try to orient themselves causing shrinkage in the materials. However it needs further exploration to properly corroborate the findings.



**Figure 3.** The variation in Shrinkage (%) of PET/nanosilica composite fibers with temperature

### ***Nylon and PBT Based CNT Fibers***

In the first experiment, a master batch sample of CNT/nylon 66 (20% of CNT concentration) was diluted to a 4% CNT concentration with fiber grade nylon 66. This material was then placed in a twin-screw extruder (at Albany international) to obtain fiber. Several problems were encountered while extruding the fiber. Overall, the fibers were formed with great difficulty. Any fiber produced was found to be very weak. The dispersion of the CNT was observed to be poor. Lumps of CNT particles were observed in specific areas of the fiber causing material discontinuity. The polymer matrix continuity needed for fiber (or film) formation was not present. Here there appears to be

poor dispersion of the CNTs in the polymer matrix. This agglomeration of CNT particles is considered to be a major problem in the extrusion of CNT containing fibers. Attempting to prepare PBT fibers with the PBT "concentrate" met with the same problems as was observed for the nylon based polymer/fiber studies. Better nanoparticle/polymer matrix melt dispersion techniques are needed.

## CONCLUSIONS

The development of nanocomposite fibers is in its infancy. There are many facets to this technology that are yet to be addressed. It is observed that the crystallinity and hence the mechanical properties of the PET was found to be influenced by the presence of the nano-silica. Higher nanosilica loading gives higher amorphous content and hence reduced crystallinity. This is manifested in observations: Increased filler loading increases the shrinkage of the composite fiber with increased temperature ramp. At higher silica loading the strength reduced moderately upto 25% but modulus was drastically reduced. The preparation of CNT reinforced fiber polymers has not yet been successful. CNT/polymer dispersion problems remain. Present studies on a new form of CNT, namely, Graphite Nano-Fibers, GNF show some promise. GNFs are commercially available in a relatively pure state and at a relatively low cost.

## ACKNOWLEDGMENT

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